



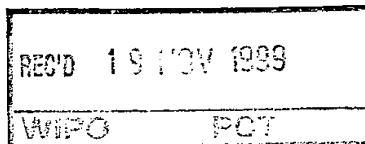
The  
Patent  
Office

PCT/YB22/03318  
09/806790



INVESTOR IN PEOPLE

#3  
The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

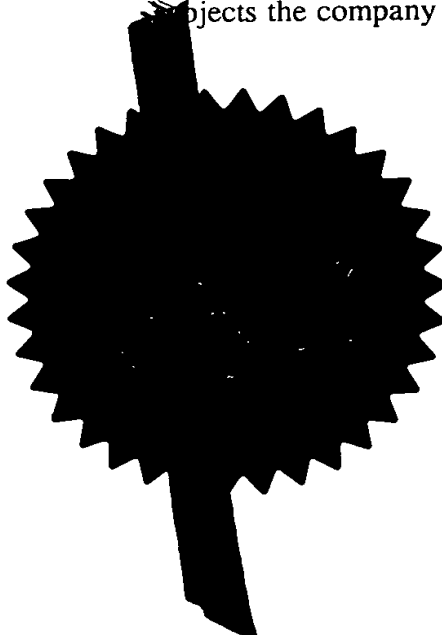


I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



*R. Mahoney*

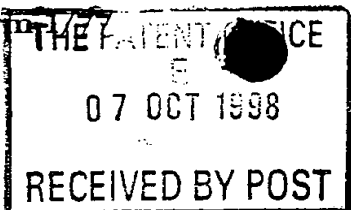
Signed

Dated 8 November 1999

**PRIORITY  
DOCUMENT**

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)





The Patent Office

7 OCT 1998

07OCT98 E395194-1 012133  
P01/7700 0.00 - 9821706.0

# Request for grant of a patent

(See the notes on the back of this form. You can also obtain an explanatory leaflet from the Patent Office to help you fill in this form)

9821706.0

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

279

2. Patent application number

(The Patent Office will fill in this part)

3. Full name, address and postcode of the or of each applicant (underline all surnames)

BRATTON GRAHAM JOHN  
154 OLD FARM AVENUE  
SIDCUP  
KENT DA15 8AL  
GB

+ 2 others

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

06636294001

4. Title of the invention

MEMBRANE STRUCTURE

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

COHEN ALAN NICOL  
2 GROVE PLACE  
TATSFIELD  
Nr. WESTERHAM  
KENT

Patents ADP number (if you know it)

TNI6 2BB 069123587001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

c) any named applicant is a corporate body.

See note (d))

NO

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

Continuation sheets of this form

2

Description

10

Claim(s)

Abstract

Drawing(s)

1

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature



Date

6/10/98

12. Name and daytime telephone number of person to contact in the United Kingdom

A. N. Cohen

01959 577172

## Warning

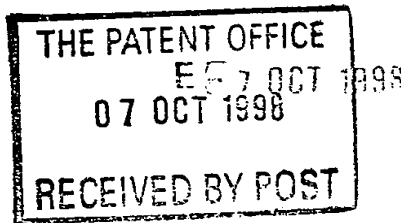
After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

## Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

2. Patent application number

(The Patent Office will fill in this part)

3. Full name, address and postcode of the or of each applicant (underline all surnames)

BUCK KARON DOREEN  
ALANCROFT  
WEST KINGSDOWN  
KENT TN15 6LH  
ENGLAND

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

06636260001

4. Title of the invention

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

c) any named applicant is a corporate body.

See note (d))

## Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description

Claim(s)

Abstract

Drawing(s)

- 
10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents  
(*please specify*)

- 
11. I/We request the grant of a patent on the basis of this application.

Signature

Date

- 
12. Name and daytime telephone number of person to contact in the United Kingdom

### Warning

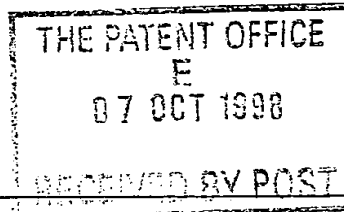
*After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.*

### Notes

- a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.*
- b) *Write your answers in capital letters using black ink or you may type them.*
- c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*
- d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*
- e) *Once you have filled in the form you must remember to sign and date it.*
- f) *For details of the fee and ways to pay please contact the Patent Office.*

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

2. Patent application number

(The Patent Office will fill in this part)

3. Full name, address and postcode of the or of each applicant (underline all surnames)

NAYLOR TIMOTHY de VILLIERS  
10 KINGSWOOD CLOSE  
ENGLEFIELD GREEN  
EGHAM  
SURREY TW20 ONQ  
ENGLAND

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

06636286001

4. Title of the invention

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

c) any named applicant is a corporate body.

See note (d))

## Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

Continuation sheets of this form

Description

Claim(s)

Abstract

Drawing(s)

- 
10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents  
(*please specify*)

- 
11. I/We request the grant of a patent on the basis of this application.

Signature

Date

- 
12. Name and daytime telephone number of person to contact in the United Kingdom

### Warning

*After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.*

### Notes

- a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.*
- b) *Write your answers in capital letters using black ink or you may type them.*
- c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*
- d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*
- e) *Once you have filled in the form you must remember to sign and date it.*
- f) *For details of the fee and ways to pay please contact the Patent Office.*



## Membrane Structure

5 The present invention relates to a membrane structure with improved performance characteristics which is particularly useful for zeolite membranes.

10 A commonly used membrane structure for separating two components consists of a tubular membrane with the mixture being passed down the tube and a separated component passing through the membrane and the other component or mixture of components passing down the tube. The tube can be bent so that it is in the form of a continuous zig-zag or other convoluted or similar configuration to increase the surface area of the tube contained in a module.

15 Alternatively or in addition there can be a plurality of tubes arranged substantially in parallel to increase the surface area of membrane without having too large a diameter of each tube or tube length.

20 In a module for use in separation or filtration processes using tubular membranes, the size and configuration of the membranes is chosen so that the optimum performance can be achieved. For a tubular membrane, the larger the diameter of the tube the greater the surface area per unit length of the tube and the lower the pressure drop down the tube, this is normally a desired criterion. However the larger the diameter of the tube, the greater the possibility, at any given flow rate of streamline flow down the tube and the greater the distance from the centre of the tube to the membrane and these will lead to a corresponding loss of performance. Whereas a narrower tube gives a lower surface area per unit length, and requires a lower flow rate to give the same degree of turbulence, but gives a higher pressure drop. In order to balance these characteristics, a series of parallel tubes in a module can be used, with the diameter of each tube chosen for optimum performance and the number of tubes chosen to have  
30 the desired surface area in the module.

5 With ceramic membranes it is cost efficient and convenient to form a plurality of tubes together in the form of a monolith. Hence monolithic assemblies of tubes have been developed wherein a single, tubular body comprises a multiplicity of smaller channels.

10 The number and shape of the inner channels can vary. For example, monoliths with 7, 19 or a greater number of channels have been developed as well as monoliths with star or other shaped channels. Typically, such designs have been developed so as to maximise the surface area per unit length of monolith, combined with minimum pressure drop whilst maintaining high overall permeability.

15 We have found that a particular arrangement of tubular membranes gives unexpectedly superior results for zeolite membranes in pervaporation over what would have been expected.

20 According to the invention there is provided a membrane structure comprising at least four tubular zeolite membranes having an internal diameter of 5 to 9 millimetres preferably 6.4 millimetres arranged within a tubular monolith having a outer diameter of 20 to 25 millimetres, preferably 20mm.

25 In practice the internal diameter will vary along the length of the tubular membrane and will vary according to membrane thickness, so the internal diameter of the tubular membranes is an approximate average along the length of the tube and the invention will encompass structures which deviate from the exact measurements in accordance with normal practice.

30 The tubular zeolite membrane is preferably formed by the methods disclosed in our co-pending patent applications PCT/GB96/00243, PCT/GB97/00928 and PCT/GB 97/00635.

Typical zeolites which can be used in the present invention include but are not limited to, 3A, 4A, 5A, 13X, X, Y, ZSM5, MPOs, SAPOs, Silicalite, b, q, etc.

- 5     The porous supports on which zeo-type membranes are formed are preferably formed of sintered ceramic powders such as alpha alumina, titania, zirconia or other suitable media which are capable of being extruded and sintered upon which the zeolite will nucleate and grow.
- 10    The present invention can be used with porous supports of any suitable size although, for large flux rates through a membrane, large pore sizes are preferred. Preferably pore sizes of 0.01 to 2,000 microns, more preferably of 0.1 to 200 and ideally of 0.1 to 20 microns are used. Pore sizes up to 300 microns can be determined by bubble point pressure as specified in ISO 4003. Larger pore sizes can be measured by
- 15    microscopic methods.

The membranes which can be used in the present invention can be formed by any method, for example by crystallisation from a gel or solution, by plasma deposition or by any other method such as electro-deposition of crystals on conducting substrates

20    e.g. as described in DE 4109037.

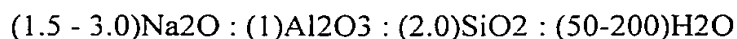
When the membrane comprising a film of zeo-type material is prepared by crystallisation from a synthesis gel, any of the methods described in the prior art can be used.

25    The synthesis gel used in the process can be any gel which is capable of producing the desired crystalline zeo-type material. Gels for the synthesis of zeo-type materials are well known and are described in the prior art given above or, for example, in EP-A-57049, EP-A-104800, EP-A-2899 and EP-A-2900. Standard text books by D W

30    Breck ("Zeolites Molecular Sieves, Structure Chemistry and Use") published by John

Wiley (1974) and P.A Jacobs and J.A Martens (Studies in Surface Science and Catalysis No. 33, Synthesis of High Silica Alumino silicate Zeolites" published by Elsevier (1987), describe many such synthesis gels. The process which can be used includes conventional syntheses of zeo-type materials, except that the synthesis is carried out in the presence of the porous support. Most commonly, gels are crystallised by the application of heat.

The membrane can be prepared by a process which comprises deposition or crystallisation from a growth medium. One method for forming the membrane preferably has a molar composition in the range of



and the method used can be used in any of the methods disclosed in the references listed above

The conditions which can be used for forming the membrane are with a temperature of the growth solution preferably in the range of 50 to 100°C and the pH can be adjusted e.g. to pH of 12.5 to 14 by addition of sodium hydroxide or ammonia. If desired the sodium ion concentration can be increased without increasing the pH by the addition of a sodium salt such as sodium chloride. The growth solution can be seeded with zeolite crystals of the desired zeolite to be synthesised. The membrane can be washed to pH neutral after membrane formation prior to any post-treatment.

The porous support can be contacted with the growth medium by immersion or by pouring the growth medium over the support with the support held substantially horizontal, either face up at the bottom of a container, or face down at the surface of the growth medium, or it can be passed over one or both sides of the support, with the support held substantially horizontal, or it can be passed over one or both sides of the support with the support held substantially vertical or the support can be in any intermediate position.

The growth medium can be kept static, stirred, tumbled or passed over or around the support, alternatively the growth medium can be passed over both sides of the support with the support held substantially horizontal or at any intermediate position.

5

Pressure may also be applied but it is usually convenient to conduct the crystallisation under autogenous pressure. Preferably the porous support is completely immersed in the growth medium; alternatively, if desired, only one surface of the support may be in contact with the growth medium. This may be useful, for example,  
10 if it is desired to produce a membrane in the form of a tube, where only the inside or outside of the tube need be in contact with the growth medium.

It may be useful if it is desired to produce a membrane containing two different zeolites, one on each side of the support. Use of such a bi-functional membrane  
15 would be equivalent to using two separate membranes, each carrying a different zeolite.

If desired, the treatment with the gel can be repeated one or more times to obtain thicker membrane coatings.

20

Preferably the porous support is pre-treated with a zeolite initiating agent. The zeolite initiating agent is preferably a cobalt, molybdenum or nickel oxide or it can be particles of a zeolite, e.g. the zeolite which it is intended to deposit on the porous support, or any combination of these. Another example of an initiating agent is a  
25 compound which can deposit a zeo-type pre-cursor material e.g. a silicic acid or polysilicic acid.

The zeolite initiation agent can be contacted with the porous support by a wet or dry process. If a dry process is used, the particles of the zeolite initiation agent can be

rubbed into the surface of the porous material, or the porous material surface can be rubbed in the particles.

Alternatively the particles of the zeolite initiation agent can be caused to flow over  
5 and/or through the porous support, or pulled into the support by means of a vacuum.

If a wet process is used, a liquid suspension of powder of the zeolite initiation agent is formed and the liquid suspension contacted with the porous support to deposit the zeolite initiation agent on the support.

10

Before contacting the surface of the porous support with the zeolite initiation agent the surface is preferably wetted with wetting agent such as an alcohol, water or a mixture of these.

15 After formation the membrane is preferably treated with a surface modifying agent which can cross link with the zeolite membrane and thus form a membrane with substantially no defects. The preferred surface modifying agents are silicic acid and silicates such as alkyl silicates e.g. tetra ethyl orthosilicate (TEOS).

20 In the present specification by silicic acid is meant monosilicic, low, medium and high molecular weight polysilicic acids and mixtures thereof.

Methods of making silicic acids are described in GB Patent Application 2269377.

25 The silicic acids used can have a "narrow" molecular weight distribution as formed or in a combination of different molecular weight ranges.

Greater flexibility can be introduced into the final membranes by treating them with a flexibilising agent by adding e.g. a hydroxy terminated polysiloxane into the silicic  
30 acid solution before treatment of the membrane.

The membrane structures of the present invention can be used in a range of separation and catalytic processes, e.g. dehydration of LPG, air, alcohols and natural gas, removing linear alkanes, olefins and substituted hydrocarbons from mixtures with  
5 branched chain compounds, e.g. in reforming, dewaxing, etc., hydrogenation and dehydrogenation of linear hydrocarbon in admixture with branched chain compounds.

The invention is described in the Example.

10

#### Example

A ceramic substrate of the structure of fig.1 of the drawing was pre-treated so as to deposit zeolite 4A powder on the inside of the channels using the following method.

15

The outer ceramic tube (1) had a diameter of 20mm and the inner tubes (2) had a diameter 6.4mm

20

An appropriate sized pipe cleaner, which had been loaded with zeolite 4A particles (nominally sized 2-5 $\mu$ m) was inserted into one channel of a porous ceramic tube 60 cm long by 20 mm overall diameter with four channels each 6.4mm diameter and fed through the bore of one channel until it emerged out of the other end (the pipe cleaner was twisted to form a stiffer rod so as to aid insertion through the tube). The pipe cleaner was pulled backwards and forwards through the channel effecting a deposit of  
25 4A particles on the internal walls of the channel. This was repeated for each of the remaining three channels.

25

By this method of powder deposition, between  $0.435 \times 10^{-4}$  and  $2.39 \times 10^{-4}$  g/cm<sup>2</sup> of powder were deposited on the total surface of the ceramic support. The total weight  
30 of powder deposited was found to vary with the pore size of the ceramic support.

### Membrane growth procedure

5 The zeolite membrane was formed on the inside of the four pre-treated channels by allowing a hydrogel suspension to be in contact with the surfaces under the conditions described below.

10 The hydrogel is formed by combining two separate solutions, (solution A) and (solution B ) to form a homogeneous suspension.

#### Solution A

15 24.49g Sodium Aluminate, 3.75g Sodium Hydroxide and 179.74g de-ionised water were mechanically shaken until dissolved. The Sodium Aluminate had an actual composition 62.48%  $\text{Al}_2\text{O}_3$ , 35.24%  $\text{Na}_2\text{O}$ , and 2.28%  $\text{H}_2\text{O}$ .

#### Solution B

20 50.57g Sodium Silicate of composition 14.21%  $\text{Na}_2\text{O}$ , 35.59%  $\text{SiO}_2$  and 50.20%  $\text{H}_2\text{O}$  was dissolved in 148.8g de-ionised water.

25 Solution A was heated to  $50^\circ\text{C}$  and added slowly to solution B which had been pre-heated to  $90^\circ\text{C}$  with stirring to ensure complete and even mixing (it is important that no lumps of hydrogel are formed). The mixture was then heated to  $95^\circ\text{C}$ . This resulted in a hydrogel having a molar composition

2.01  $\text{Na}_2\text{O}$  :  $\text{Al}_2\text{O}_3$ : 2.0  $\text{SiO}_2$  : 143.10  $\text{H}_2\text{O}$

30 The pre-treated tube was wetted by immersing it in deionised water for 15 seconds. The tube was then suspended vertically above the bottom of the growth vessel. Hot



hydrogel was then added to the growth vessel, care being taken to ensure that all the air was expelled from the channels .

The growth vessel was sealed and heated to 100°C for 5 hours.

5

After 5 hours the tube was removed from the growth vessel, allowed to cool slightly and then removed and washed clean using deionised water over a period of 16 hours. The ceramic tube was then dried at 100°C for 6 hours.

10 X-ray Analysis showed this to be a Zeolite 4A.

15 A mixture of polysilicic acids of mean molecular weight of about 800 was diluted with ethanol to 5% wt. solids. 500ml. of this solution was circulated over the feed side of the membrane and drawn through the membrane to treat the surface whilst being heated to 70° C., with vacuum for 5 hours to cross-link the silicic acid in the pores of the membrane.

20 A comparison of the performance of the four channelled monolith with that of a single narrow tube in water separation form a water/isopropanol mixture at 70°C. Care was taken to ensure that the tubes were tested under identical conditions of turbulence of the feed solution and the results shown below.

- 10 -

5	Tube Type	Water Flux	Number of	Tube price per	£/Kg water
		Kg/ m <sup>2</sup> /day At Re8582 and 2% wt Water/ IPA at 70°C	tubes per m <sup>2</sup>	m <sup>2</sup> at £100 each	removed
	4 Channel	21	22	2200	200
	Narrow bore	41	100	10,000	243.9

10

The tube dimensions were

15		Tube Diameter	Tube Inner	Tube area per
		mm	Circumference	58cm length
	4 channel	4 x 6.4	7.92	459
	Narrow Bore	1 x 5.5	1.728	100.2

20 As can be seen the four tube configuration is surprisingly superior in performance and cost per unit area of membrane.

1/1

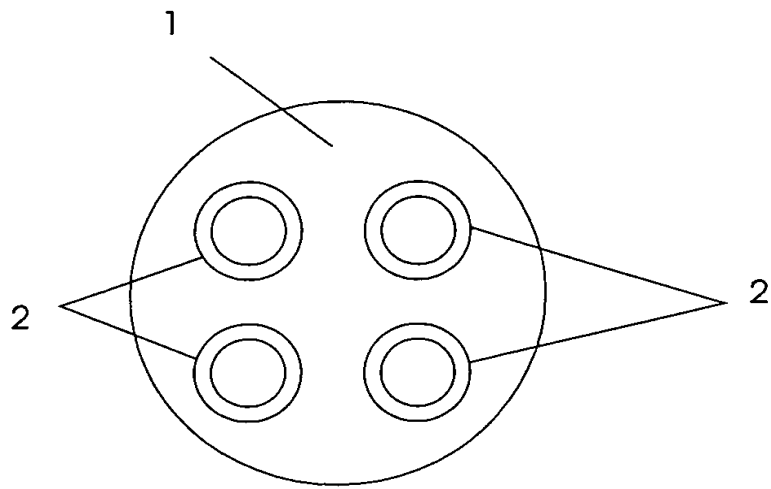


Fig. 1

PCT NO : GB 99 / 03318

Form 23/77 : 7.10.99

AGENT : A. N. Cohen